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A Comprehensive Study of Polypropylene/Organoclay Nanocomposites : Preparation, Material Characterisation and Numerical Simulation

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1. Introduction

The development of polymer/clay nanocomposites faces the enormous challenge to offer the consistent mechanical properties for the end users. Such obstacle is derived from the lack of in-depth knowledge of the effects of the individual processing parameter and manufacturing methodology. Furthermore, a more reliable numerical approach to predict their mechanical properties is still at its infant stage despite the available micromechanical models in conventional composite systems and the representative volume element (RVE) models to greatly simplify the filler's geometry, shape and aspect ratio. This paper elaborates a comprehensive study on the determination of optimal formulation in the melt compounding, material characterisation and real morphology-based numerical simulation of polypropylene (PP)/organoclay nanocomposites in order to offer a greater insight for the researchers and engineers of properly handling the nanocomposites.

2. Preparation and Material Characterisation

Three commercial grades of polypropylene (PP), namely PP-Co M710 (Melt Flow Index=0.6g/10min), PP-Hom Y130 (MFI=4.0g/10min) and PP-Hom H380F (MFI=25 g/10 min) were supplied by Clariant NZ Ltd. NANOLIN™ organoclay (DK1N, DK2 and DK4 with interlayer spacing d_{001}=2.29, 2.25 and 3.56 nm, respectively), modified with octadecylammonium salt, was purchased from Zhejiang Fenghong Clay Chemicals Co., Ltd, China. Maleic anhydride grafted PP (MAPP) Exxelor™ PO1020 (MA content: 0.5-1 wt%, MFI=~430g/10 min) was selected as the compatibiliser from ExxonMobil Chemical (Germany). Design of experiments (DoE) [1,2] was employed to generate the factorial and mixture design for the optimal formulation. Table 1 elaborates the factors and levels in the nine trials of the DoE work with the assumption of no factorial interactions. PP/organoclay nanocomposites were prepared by twin screw extrusion of PP and MAPP pellets with downstream clay feeding and then recompounded to extend the residence time. Finally dried nanocomposites were injection moulded to prepare mechanical test samples. The material preparation and DoE formulation layout can be found in details elsewhere [3].

Table 1 Four factors and three levels used in L_9 DoE layout

Factor	Level		
	1	2	3
A: Clay type	DK1N	DK2	DK4
B: Clay content (wt%)	3	5	10
C: MAPP content (wt%)	5	10	20
D: PP type	PP-Co M710	PP-Hom Y130	PP-Hom H380F

A Philips CM 12 transmission electron microscope (TEM) was utilised to investigate the morphology and level of clay dispersion in nanocomposites at 120kV. Ultra thin TEM samples of 70nm in thickness were prepared in a longitudinal melt flow direction by a Hitachi S-4700 ultramicrotome at -80°C. Tensile, flexural and impact tests were conducted according to ASTM D638, D790 and D6110, respectively and final results were based on the average data of five samples in each case.

3. Numerical Simulation Technique

The elastic moduli of nanocomposites were numerically predicted by an object-oriented finite element code (OOF 2.0.4) [4] based on mapping the real micro/nanostructures of clay platelets in TEM imaging analysis. OOF 2.0.4 was installed in a Fedora Red Hat Core 4 Linux system. The finite element analysis was conducted on a Dell INSPIRON™ 8600 laptop with the Windows XP and Linux dual boot system using 1.6 GHz processors and 2 GB RAM. The constituent properties of PP/organoclay nanocomposites are given in detail in reference [5].

4. Results and Discussion

The best combination of factors to enhance each of the mechanical properties has been determined in Table 2, along with the respective compositions and estimates of error variance. Such material formulations were derived from the "larger-the-better" characteristics in Taguchi DoE method [1,2]. Since DoE results show significant effects of PP type and clay content on the properties, particularly with PP-Hom H380F proving to be the best performing PP grade, the final optimal formulation was based on using this PP, MAPP and DK4 clay of 3 wt%, 5 wt%, 8 wt% and 10 wt% (weight ratio of MAPP: organoclay remained as 2:1). The mixtures were then subjected to identical sample preparation conditions.

Table 2 Summary of preferred formulations for improving the mechanical properties of PP/organoclay nanocomposites

Larger-the-better L_9 DoE response (Normalised)		Preferred factorial level combination	Composition (wt%)	Estimate of error variance
Tensile properties	Tensile modulus	$A_3B_3C_3D_3$	DK4/MAPP/H380F (10/20/70)	0.35
	Tensile strength	$A_3B_2C_2D_3$	DK4/MAPP/H380F (5/10/85)	0.04
Flexural properties	Flexural modulus	$A_3B_3C_3D_3$	DK4/MAPP/H380F (10/20/70)	0.31
	Flexural strength	$A_2B_3C_1D_3$	DK2/MAPP/H380F (10/5/85)	0.05
Impact properties	Impact strength	$A_1B_1C_1D_3$	DK1N/MAPP/H380F (3/5/92)	9.70

Fig.1 shows that the addition of clay particles enhances the overall mechanical properties of optimally formulated nanocomposites. Tensile modulus shows a relatively monotonic improvement with the increase of clay content (maximum enhancement being 41 % with clay content of 10 wt %). Tensile strength also increases up to 16%, but beyond 3 wt % clay, it more or less levels off regardless of the clay content. Impact strength achieves a 50 % improvement at the clay content of 3 wt % but then declines to be the same as that of neat PP at 10 wt % clay. Such decline might have resulted from both clay agglomeration at higher content levels, coupled with growing brittleness with the proportional increase in the amount of MAPP.

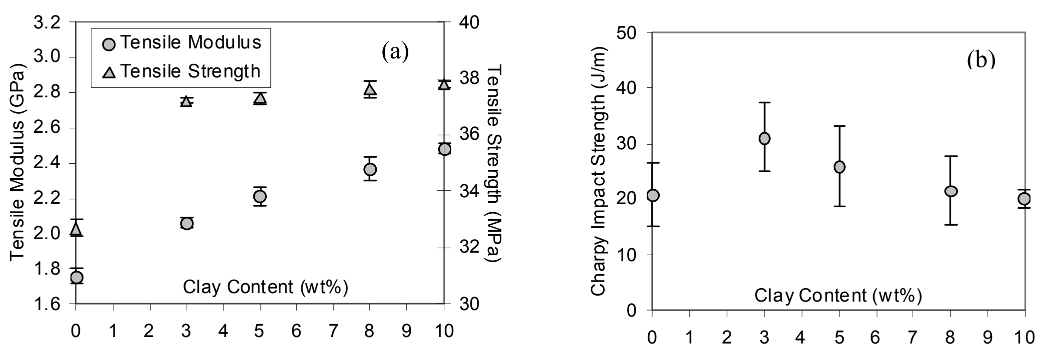

Fig.1 Mechanical properties of optimal PP/organoclay nanocomposites (weight ratio WR=2:1): (a) tensile properties and (b) impact strength.

Partially exfoliated and intercalated structures of clay platelets are depicted in Fig.2, which helps to improve the mechanical properties of nanocomposites. The lower clay content appears to produce a better clay dispersion. Clay platelets with the lateral dimension of 200-500 nm are manifested in skewed and curved formations. Owing to the compatibiliser role of MAPP, the tactoid size of clay particles appears to be reduced at a high clay content despite signs of localised agglomeration.

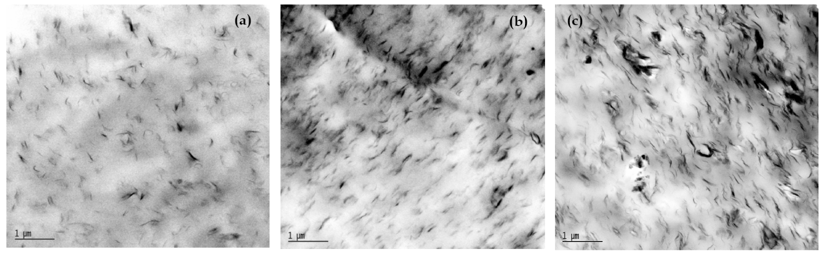

Figure (2) : TEM micrographs of optimal PP/organoclay nanocomposites (WR=1:2) at 15000× magnification with the clay contents: (a) 3 wt %, (b) 5 wt % and (c) 10 wt %.

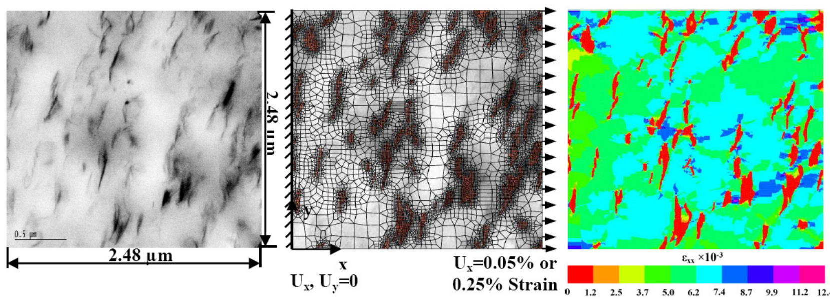

Figure (3) : A Typical OOF representation and tensile strain contour of 5 wt % filled PP/organoclay nanocomposites.

The OOF modelling (a typical example shown in Fig. 3) results capture well the linearly increasing trend of elastic modulus with an increased clay content, and are in good agreement with the experimental data, Fig.4. The experimental data have also been compared with the typical Halpin-Tsai [6] and Hui-Shia [7] models in the unidirectional platelet alignment, as well as their laminate hybrid models [5] in 3-D random orientation with various clay aspect ratios (5~80). At a fixed aspect ratio, each curve for the random orientation lies below the corresponding one for the unidirectional alignment, leading to sizeable reductions in composite stiffness. Such modulus reduction becomes more pronounced for Halpin-Tsai laminate hybrid model compared to the unmodified Halpin-Tsai model for discontinuous fibre-like fillers, Figs. 4(a)-(b). Nevertheless, Hui-Shia laminate hybrid model demonstrates less modulus reduction in contrast to unmodified Hui-Shia model for the disk-like platelet filler geometry with the biaxial reinforcement, Figs. 4(c)-(d). It is evident that platelets do not tend to be as sensitive as fibres to the orientation states, which can benefit the nanocomposite system requiring an effective multi-directional reinforcement.

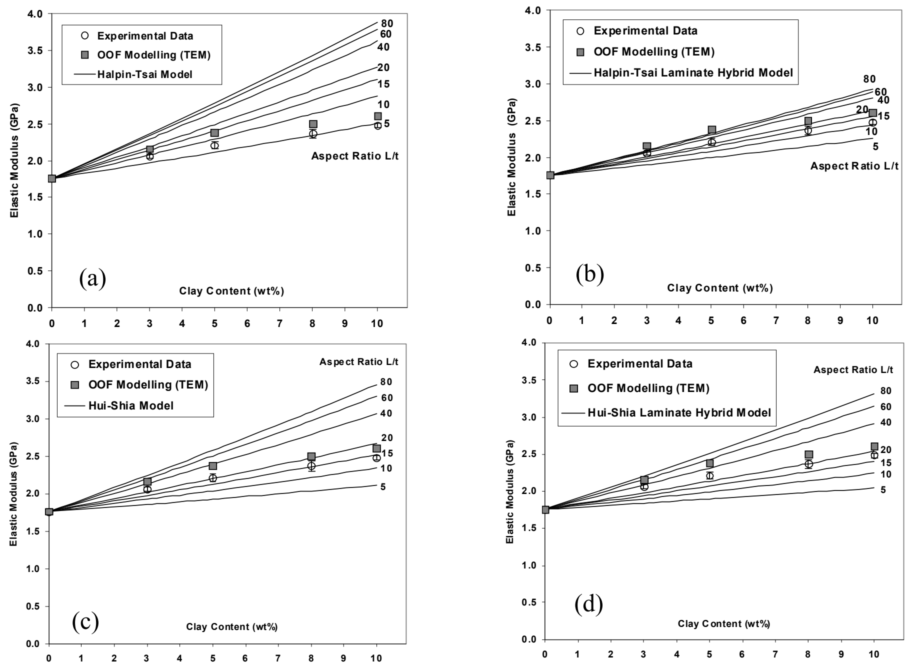

Figure (4) : Comparisons of experimental data, OOF (TEM) results and composites theoretical models.

5. Conclusions

A comprehensive study of PP/organoclay nanocomposites has been described briefly in this paper, which clearly establishes the merits of using the design of experiments to achieve the optimal formulation for the enhancement of their mechanical properties. These properties benefit from a mixture of intercalated and exfoliated clay structures, as shown in the TEM material characterisation. The implementation of Object Oriented Finite element modelling technique reflects an alternative numerical approach that can predict well the elastic moduli of PP/organoclay nanocomposites in comparison to the predictive micromechanical models of conventional composite systems.

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